



Time and space variations in Cu and Zn isotope compositions of SPM and sediments in an estuarine environment (The Scheldt estuary)

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Cu and Zn isotope biogeochemistry has already been applied to study oceanic environments via deep ocean carbonates (Pichat *et al.*, 2003), sediment trap samples, sediments and Fe-Mn nodules (Maréchal *et al.*, 2000). So far, no study has been published on Cu and Zn isotopic fractionation in estuarine environments, while estuaries represent fundamental stages in the hydrological and geochemical cycles of these metals. Estuarine environments are characterized by strong physico-chemical gradients (pH, eH, dissolved oxygen,...) related to marine- and fresh waters mixing and important biological activity (Paucot *et al.*, 1997). Those physico-chemical gradients induce important redistribution of trace elements between dissolved and particulate phases. We therefore anticipate fractionation of Cu and Zn isotopes to occur in estuaries with a greater extent than in open ocean.

This study focuses on results of Cu and Zn elemental and isotopic compositions of centrifuged suspended particulate matter (SPM) of the Scheldt estuary (Belgium and Netherlands, campaign Eurothroph April 2003).

Samples were collected at 6 stations along a 100 km transect (Belgica vessel). Present results are compared with previous data obtained on surface sediments and SPM of November 2002 (Petit *et al.*, 2004).

Prior to standard HF+HNO₃ dissolution procedure, organic matter was digested by

repeated additions of concentrated H_2O_2 . Separation of Cu, Fe and Zn was carried out by one step ion-exchange chromatography on AG-MP1 resin. To avoid fractionation artifacts, the full recovery of Cu, Fe and Zn from different matrix samples (basalt, sediment and limestone) was quantitatively verified. Total blanks were negligible: 1.5; 11 and 4.5 ng for Cu, Fe and Zn, respectively. Cu and Zn isotopic ratios were measured with a "Nu-Plasma" MC-ICP-MS (ULB). Instrumental mass bias was corrected by simultaneous standard-sample bracketing and external normalisation, assuming an exponential mass fractionation law. Reference materials were Zn JMC and Cu NIST SRM 976 standards. The Nu plasma allowed ^{60}Ni to be simultaneously monitored and used for systematic correction on ^{64}Zn . Reference materials were repeatedly measured, giving a long-term reproducibility of ± 0.07 per mil for $\delta^{65}\text{Cu}$ and $\delta^{66}\text{Zn}$ (2σ , $n=158$ over 13 analysis sessions). Average total beam intensities are 6 V/ppm. The whole methodology has been checked for spectral and non-spectral interferences, as well as artifacts related to analyte-to-dopant concentration ratios. Each sample was analyzed for at least three concordant replicates.

Profiles of concentration vs. salinity show expected Cu and Zn enrichments in SPM in the upper estuary and a non conservative decrease seaward. As a whole, Cu and Zn concentration range from 100 ppm (at 5 psu) to 0.6 ppm (at 30psu) and from 600 ppm (at 5 psu) to 100 ppm (at 30psu), respectively. $\delta^{66}\text{Zn}$ values of SPM describe a positive linear correlation with salinity, i.e. a "conservative" trend from 0.24 ± 0.07 per mil at 1 psu to 0.61 ± 0.01 per mil at 30 psu. In contrast, $\delta^{65}\text{Cu}$ shows rapid variations from 0.00 ± 0.03 per mil at 1 psu to $+0.99 \pm 0.03$ per mil at 3 psu down to -0.78 ± 0.02 per mil at 13 psu. Those contrasted behavior and amplitude of variation may reflect differences in reactivity of species related to Cu and Zn speciation, as can be revealed by acidimetric titration. When both seasons are considered, $\delta^{65}\text{Cu}$ variations in the SPM are more important in April 2003 relative to November 2002 (1.44 against 0.37 per mil, respectively), while $\delta^{66}\text{Zn}$ results show no significant seasonal change. Compared to sediments, SPM samples are systematically enriched in light Cu and Zn isotopes in the lower estuary (downstream the Maximum Turbidity Zone) where sediments show a regular increase in $\delta^{66}\text{Zn}$ and $\delta^{65}\text{Cu}$ seaward.

This study provides a stepping-stone for further investigation of exchange processes of metals between particulate and dissolved phases in estuarine environment. These preliminary results pinpoint significant spatial and temporal variations in isotopic compositions of particulate Cu and Zn as well as contrasted isotopic signatures between sediments and suspended particulate matter. Cu and Zn isotopic variations within estuarine particulate phases suggest to revisit the use of particulate Cu and Zn for constraining their biogeochemical, behavior, so far essentially studied via the dissolved phase.

References:

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